

Japanese Kokai Patent Application No. Hei 7[1995]-26147

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Translated from Japanese by the Ralph McElroy Co., Custom Division  
P.O. Box 4828, Austin, Texas 78765 USA

Code: 720-54051  
Ref.: Weitz

JAPANESE PATENT OFFICE  
PATENT JOURNAL  
KOKAI PATENT APPLICATION NO. HEI 7[1995]-26147

Technical Disclosure Section

Int. Cl. <sup>6</sup> :	C 08 L 83/07 83/05 C 09 D 183/07 C 09 J 183/07
Application No.:	Hei 6[1994]-120530
Application Date:	May 10, 1994
Publication Date:	January 27, 1995
Priority:	
No.:	Patent Application No. Hei 5[1993]-132659
Date:	May 10, 1993
Country:	Japan
No. of Claims:	2 (Total of 6 pages; FD)
Examination Request:	Not requested

HEAT-CURABLE SILICONE ELASTOMER COMPOSITION

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[There are no amendments to this patent.]

## Abstract

### Constitution

Heat-curable silicone elastomer composition containing (A) thermoplastic resins containing platinum catalysts and hydrosilylation reaction control agents, (B) organopolysiloxanes having two or more unsaturated aliphatic hydrocarbon groups directly bonded to the silicon atoms in the molecule, and (C) organohydrogenpolysiloxanes having two or more hydrogen atoms directly bonded to the silicon atom in the molecule.

### Effect

This composition has excellent storage stability. Namely, this composition shows good storage stability for a long period of time at room temperature, without the curability lowering at high temperature.

## Claims

1. Heat-curable silicone elastomer composition containing (A) thermoplastic resins containing platinum catalysts and hydrosilylation reaction control agents, (B) organopolysiloxanes having two or more unsaturated aliphatic hydrocarbon groups directly bonded to the silicon atoms in the molecule, and (C) organohydrogenpolysiloxanes having two or more hydrogen atoms directly bonded to the silicon atoms in the molecule.

2. Method for the manufacture of cured products obtained by heat curing the composition of Claim 1.

Detailed explanation of the invention

[0001]

## Industrial application field

The present invention concerns heat-curable silicone elastomer compositions curable by hydrosilylation and useful for potting materials, coating materials, adhesives, liquid injection molding materials, etc.

[0002]

## Prior art

The heat-curable silicone elastomer compositions curable by hydrosilylation can be cured rapidly with the advantage of no by-product formation; thus, they are widely used for potting materials, coating materials, adhesives, liquid injection molding materials, etc. However, the activity of the catalysts used for the hydrosilylation is difficult to control; thus the heat-curable silicone elastomer compositions are usually used in two-liquid form. When such two-liquid compositions are used for coatings, the components have to be mixed on site; thus, using them is cumbersome, with possible workability problems.

[0003]

Thus, there have been proposals of heat-curable silicone elastomer compositions in single-liquid form, containing

hydrosilylation reaction control agents for control of the catalyst activity at room temperature. Such control agents are, e.g., nitrile compounds; carboxylates; metal compounds such as stannous and mercuric compounds, etc.; sulfur compounds; benzotriazole; acetylene compounds; hydroperoxides, etc. Such single-liquid compositions are stable at room temperature. However, when such control agents are added to obtain long-term storage stability, the compositions show problems of significantly decreased curability. For maintaining curability, the control agent content has to be reduced, resulting in reduced composition storage stability.

[0004]

Heat-curable silicone elastomer compositions in single-liquid form have been developed by adding platinum catalysts sealed in a silicone resin of a certain softening point (hereafter catalyst-containing resins) to the elastomer compositions, without addition of the reaction control agents (Japanese Kokoku Patent No. Sho 53[1978]-41707; Japanese Kokai Patent Application No. Sho 58[1983]-37053). However, in this method, when the platinum catalyst is sealed in the silicone resin, a small amount of catalyst adheres to the resin surface, and because of said catalyst adhering to the surface of the catalyst-containing resins, the elastomer curing is accelerated during storage. The obtained single-liquid elastomer compositions have poor storage stability (here, storage stability refers to no deterioration of long-term storage stability at room temperature and curability at high temperature).

[0005]

Compositions have been proposed with separate additions of the above catalyst-containing resins and hydrosilylation reaction control agents (Japanese Kokai Patent Application No. Hei 4[1992]-46962). Such heat-curable silicone elastomer compositions in single-liquid form have excellent long-term stability at room temperature. However, to obtain such storage stability, the reaction control agents have to be added to the compositions in large quantities. As a result, over time, the reaction control agents penetrate into the catalyst-containing resins; thus, the compositions lose storage stability and have reduced curability at high temperature, leading to no practical usability of the compositions.

[0006]

Problems to be solved by the invention

It is an objective of the present invention to provide heat-curable silicone elastomer compositions having excellent storage stability with good stability at room temperature over a long period of time, yet without losing high-temperature curability.

[0007]

Means to solve the problems

As a result of an investigation of ways to achieve the above objectives, it has been discovered that heat-curable silicone elastomer compositions with excellent storage stability can be obtained by adding thermoplastic resins containing hydrosilylation reaction control agents and platinum catalysts for hydrosilylation reaction. Namely, the elastomer compositions are stable at room temperature over a long period of time, yet good curability at high temperature is maintained. Thus, the present invention is attained.

[0008]

Namely, the present invention provides heat-curable silicone elastomer compositions containing (A) thermoplastic resins containing platinum catalysts and hydrosilylation reaction control agents, (B) organopolysiloxanes having two or more unsaturated aliphatic hydrocarbon groups directly bonded to the silicon atoms in the molecule, and (C) organohydrogenpolysiloxanes having two or more hydrogen atoms directly bonded to the silicon atoms in the molecule.



[0009]

(A) Thermoplastic resins containing platinum catalysts and reaction control agents

The thermoplastic resins containing platinum catalysts and hydrosilylation reaction control agents of component (A) are added for crosslinking of the organopolysiloxanes having unsaturated aliphatic hydrocarbon groups of component (B) with the organohydrogenpolysiloxanes of component (C) by hydrosilylation.

[0010]

Platinum catalysts

The platinum catalysts include platinum and platinum compounds, and conventional platinum catalysts used for hydrosilylation may be used here, e.g., platinum, chloroplatinic acid, platinum sulfide, sodium chloroplatinate, platinum-olefin complexes, chloroplatinic acid-alkenyl group-containing organosiloxanecomplexes, etc. Such platinum catalysts may be supported on inorganic compounds such as silica, carbon black, alumina, titanium oxide, etc., or used as alcohol solutions. The platinum catalysts may be used alone or as mixtures thereof. Among such platinum catalysts, for high catalytic activity chloroplatinic acid-divinylsiloxane complexes are preferred.

[0011]

The platinum catalyst content based on 100 parts by weight thermoplastic resin is less than 50 parts by weight, preferably 0.1-10 parts by weight. Excessive content makes hydrosilylation reaction control difficult, and if not enough, curability is not satisfactory.

[0012]

#### Hydrosilylation reaction control agents

The hydrosilylation reaction control agents may be selected from conventional ones, e.g., phosphorus compounds such as triphenylphosphine, etc.; nitrogen-containing compounds such as tetramethylethylenediamine, benzotriazole, etc.; acetylene compounds such as propargyl alcohol, 1-ethynylcyclohexanol, 1,1-dimethyl-3-butynol, etc.; hydroperoxide compounds such as t-butyl hydroperoxide, etc.; tin compounds such as dibutyltin dilaurate, tin octylate, etc.; mercury compounds such as mercury(I) chloride, etc. They may be used alone or as mixtures thereof. Among such compounds are preferably acetylene compounds, more preferably organic compounds having alkynyl groups and alcoholic hydroxy groups.

[0013]

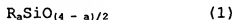
The hydrosilylation reaction control agent content based on 1 mol platinum atoms of the platinum catalysts should be 100 mol or less, preferably 1-10 mol. A higher content results in

compositions without sufficient curability, while not enough makes the hydrosilylation reaction control difficult, with deterioration of storage stability at room temperature.

[0014]

#### Thermoplastic resins

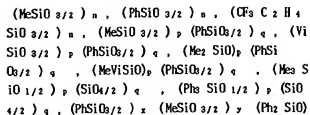
The thermoplastic resins may be chosen from organic polymers, e.g., vinyl polymers such as polyethylene, polystyrene, etc.; or condensation polymers such as polyamides, polyesters, etc. They may be used alone or as mixtures thereof. Among them, silicone resins are preferred, more preferably silicone resins of average composition formula (1):



(in the formula, R is a monovalent organic group;  $a = 1-1.8$ , preferably  $1-1.5$ ). In formula (1), the monovalent organic groups represented by R include aliphatic unsaturated group-free substituted or unsubstituted hydrocarbon groups of 1-12 carbon atoms, preferably 1-8 carbon atoms, e.g., alkyl groups such as methyl group, ethyl group, propyl group, etc.; aryl groups such as phenyl group, tolyl group, etc.; organic groups whose hydrogen atoms are partially or wholly substituted by halogen atoms or cyano groups such as trifluoropropyl group, chloromethyl group, cyanoethyl group, etc. Such organic groups may be used alone or as combinations thereof. In the formula, R containing 50 mol% or more phenyl group is preferred.

[0015]

Specific examples of preferred silicone resins represented by formula (1) are,



2

(in the formulas, p, q, x, y and z independently represent whole numbers of 1 or more, and n, p + q, and x + y + z represent 10 or more; Me is methyl group; Ph phenyl group, Vi vinyl group). Such silicone resins may be used alone or as mixtures thereof.

[0016]

The thermoplastic resins are used for preventing hydrosilylation reaction during storage at room temperature by sealing the platinum catalysts; thus, the resins should be in solid form and stable at room temperature. The resins should have a melting point or softening point at 40-150°C. With the resin melting point or softening point too low, the catalysts may diffuse into the compositions during storage, causing curing by hydrosilylation reaction. On the other hand, with the resin melting point or softening point too high, the curing temperature of the compositions are high; thus, desired curability is not

attained. Furthermore, the thermoplastic resins should not be eluted into compositions after preparation.

[0017]

Such thermoplastic resins containing platinum catalysts and reaction control agents should be uniformly dispersed into the compositions when used. While not restricted in any particular way, the thermoplastic resins may be in fine powder or particle form, with diameter 0.1  $\mu\text{m}$  to 1 mm, preferably 1-100  $\mu\text{m}$ . The fine powders and granules may be prepared by a usual manner, e.g., spray drying, etc.

[0018]

The above platinum catalyst- and reaction control agent-containing thermoplastic resin (A) content in the compositions is 1-1000 ppm, preferably 10-100 ppm as platinum to component (B).

[0019]

(B) Unsaturated aliphatic hydrocarbon group-containing organopolysiloxanes

The organopolysiloxanes having two or more unsaturated aliphatic hydrocarbon groups bonded to the silicon atoms in the molecule is the main agent of the heat-curable silicone elastomer compositions of the present invention.

[0020]

Such unsaturated aliphatic hydrocarbon groups of the organopolysiloxanes are usually of 2-10, preferably 2-4 carbon atoms, e.g., alkenyl groups such as vinyl group, allyl group, isopropenyl group, etc., while vinyl group is preferred. They may be included alone or in combinations. Such unsaturated aliphatic hydrocarbon groups may be bonded to silicon atoms at the molecular chain ends or in the middle of the molecular skeleton. The organic groups other than the unsaturated aliphatic hydrocarbon groups of organopolysiloxanes are usually substituted or unsubstituted monovalent hydrocarbon groups of 1-12, preferably 1-8 carbon atoms, e.g., alkyl groups such as methyl group, ethyl group, propyl group, etc.; aryl groups such as phenyl group, tolyl group, etc.; organic groups whose hydrogen atoms are partially or wholly substituted by halogen atoms or cyano groups, such as trifluoropropyl group, chloromethyl group, cyanoethyl group, etc. The organic groups other than the unsaturated aliphatic hydrocarbon group in the organopolysiloxane molecules is not limited to one type.

[0021]

The organopolysiloxane structures may be in linear, branched, or cyclic form, while linear structure is preferred. The linear structure may also contain partial branching or a cyclic skeleton.

[0022]

In the case of liquid compositions, the organopolysiloxanes should have a degree of polymerization of 20-2000, preferably 50-500. On the other hand, for the compositions in nonliquid rubber form, the organopolysiloxanes should have a degree of polymerization of 2000 or greater.

[0023]

(C) Organohydrogenpolysiloxanes

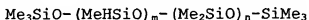
The organohydrogenpolysiloxanes having 2 or more hydrogen atoms bonded to the silicon atoms of the molecules of component (C) are the components undergoing crosslinking by hydrosilylation with the organopolysiloxanes of component (B). Other than the hydrogen atoms, the organic groups in the organohydrogenpolysiloxanes are aliphatic unsaturated bond-free substituted or unsubstituted monovalent hydrocarbon groups of usually 1-12, preferably 1-8 carbon atoms, e.g., alkyl groups such as methyl group, ethyl group, propyl group, etc.; aryl groups such as phenyl group, tolyl group, etc.; organic groups whose hydrogen atoms are partially or wholly substituted by halogen atoms or cyano groups, such as trifluoropropyl group, chloromethyl group, cyanoethyl group, etc. The organic groups other than the unsaturated aliphatic hydrocarbon group in the organohydrogenpolysiloxane molecules is not limited to one type.

[0024]

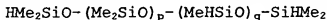
The organopolysiloxane structures may be in linear, branched, or cyclic form, while linear structure is preferred. The linear structure may also contain partial branching or a cyclic skeleton.

[0025]

The above organohydrogenpolysiloxanes should have a degree of polymerization of 3-300, preferably 5-100. Such organohydrogenpolysiloxanes can be exemplified by the formulas given below with Me representing a methyl group:

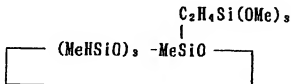


(In the formula, m is a whole number of 2 or more; n a whole number of 0 or more; m + n being 3-100);



(In the formula, p is a whole number of 0 or more; q a whole number of 0 or more; p + q being 3-100), and

[structure 1]



The organohydrogenpolysiloxane content in the compositions should be 1/10 to 12/1, preferably 1/1-3/1 as the hydrogen atoms bonded



to the silicon atoms in the organohydrogenpolysiloxane/unsaturated aliphatic hydrocarbon groups bonded to silicon atoms in the (B) component organopolysiloxane molecule molar ratio. The component (C) may be used alone or as mixtures thereof.

[0026]

Other compounding agents

If needed, the compositions of the present invention may also contain fillers such as silica fine particles, calcium carbonate, etc., heat-resisting agents such as iron oxide, etc.; fire retardants such as carbon black, etc.; tackifiers, thixotropic agents, etc.

[0027]

Preparation of compositions

The compositions of the present invention can be obtained as heat-curable silicone elastomer compositions by uniform mixing of components (A)-(C) and optionally other compounding agents under a dry atmosphere. Such preparation may be done by usual kneaders such as a kneader, roll mill, etc.

[0028]

#### Application examples

Next, the present invention is explained in detail with application examples. However, the present invention is not limited to such application examples. In the examples, H/Vi means the molar ratio of hydrogen bonded to silicon atoms in the organohydrogenpolysiloxanes of component (C)/vinyl groups bonded to silicon atoms in the organopolysiloxanes of component (B). Parts are by weight.

[0029]

(A) Preparation example of thermoplastic resins containing platinum catalysts and reaction control agents

#### Catalyst (1)

100 g silicone resin of softening point 80°C (obtained by hydrolysis of a mixture of 70 mol% phenyltrichlorosilane, 25 mol% methyltrichlorosilane, and 5 mol% diphenyldichlorosilane) were dissolved in a glass container in 500 g dichloromethane, followed by mixing with 10 g toluene solution of platinum complex (obtained by neutralizing a mixture of chloroplatinic acid and divinyltetramethyldisiloxane with sodium bicarbonate) and 0.5 g 1-ethynylcyclohexanol, keeping the resulting mixture overnight, and spray drying (inlet temperature 90°C, outlet temperature 40°C) to obtain 60 g silicone resin fine particles containing a

platinum catalyst (average particle diameter 20  $\mu$ ), as catalyst (1) with platinum content 0.4%.

[0030]

Catalyst (2)

Process for catalyst (1) was repeated using 0.34 g 1,1-dimethyl-3-butynol instead of 1-ethynylcyclohexanol to obtain 60 g silicone resin containing platinum complex, etc., as fine particles of average diameter 20  $\mu$ , as catalyst (2) with platinum content 0.4 wt%.

[0031]

Catalyst (3)

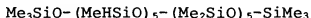
Process for catalyst (1) was repeated without using 1-ethynylcyclohexanol to obtain 60 g silicone resin containing platinum complex, etc., as fine particles of average diameter 20  $\mu$ , as catalyst (3) with platinum content 0.5 wt%.

[0032]

#### Application Example 1

A base compound was prepared by mixing 100 parts  $\alpha,\omega$ -divinylmethylpolysiloxane of average degree of polymerization 500 with 20 parts fumed silica of specific surface area 170 m<sup>2</sup>/g with surface hydrophobization by trimethylsiloxy

units [carried out] by treatment with hexamethyldisilazane. With 100 parts of this base compound were mixed 2.0 parts of the siloxane of formula:



(in the formula, Me is a methyl group) at H/Vi = 2.7 and 0.5 g of the catalyst (1) prepared above, and the resulting uniform mixture was kneaded by passing through a 3-roll mill to obtain composition I.

[0033]

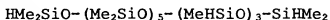
#### Comparative Example 1

Application Example 1 was repeated using catalyst (3) instead of catalyst (1) to obtain comparative composition I.

[0034]

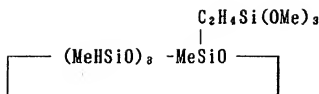
#### Application Example 2

A base compound was prepared by mixing 100 parts of  $\alpha,\omega$ -divinyldimethylpolysiloxane of average degree of polymerization 450 with 30 parts fumed silica of specific surface area 130 m<sup>2</sup>/g with surface hydrophobization by trimethylsiloxy units by treatment with hexamethyldisilazane. With 100 parts of this base compound were mixed 1.5 parts of the siloxane of formula:



(in the formula, Me is a methyl group) and 1.0 part siloxane represented by formula:

[structure 2]



(in the formula Me is a methyl group) at H/Vi = 2.4 and 0.5 g of the catalyst (2) prepared above, and the resulting uniform mixture was kneaded by passing through a 3-roll mill to obtain composition II.

[0035]

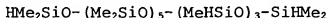
#### Comparative Example 2

Application Example 2 was repeated by mixing the base compound with 0.05 g toluene solution of divinyltetramethyldisiloxane-platinum complex (platinum content 0.5 wt%) instead of catalyst (2) and 0.8 g 1,1-dimethyl-3-butynol to obtain comparative composition ii.

[0036]

A base compound was prepared from 100 parts dimethylpolysiloxane uncured rubber of degree of polymerization 6000 terminated by dimethylvinylsilyl groups at both ends (vinyl content = 0.0020 mol/100 g),  $\alpha$  with the average polymerization degree of 20, 10 parts  $\omega$ -dihydroxydimethylpolysiloxan, and 40

parts fumed silica of specific surface area 300 m<sup>2</sup>/g by kneading in a kneader at 160°C for 4 h. With 100 parts of this base compound were mixed 0.5 part siloxane



(in the formula, Me is a methyl group) to H/Vi = 2.6 and 0.5 g catalyst (2) and the resulting uniform mixture was kneaded by passing through a 3-roll mill to obtain composition III.

[0037]

### Comparative Example 3

Application Example 3 was repeated by adding base compound with 0.35 g 1,1-dimethyl-3-butynol and catalyst (3) instead of catalyst (2) to obtain comparative composition iii.

[0038]

### Evaluation of the compositions

The compositions obtained from application examples and comparative examples were evaluated by the following methods. Results are given in Table I.

### Curing characteristics

The curing characteristics of each composition obtained from application examples and comparison examples were evaluated at 150°C using a rheometer. For each composition, the time to reach a certain torque was measured and compared. In Table I, T10 is

the time needed to reach 10% maximum torque; T90 is the time needed to reach 90% maximum torque. Compositions stored at 25°C for a certain period were measured for curing characteristics at 150°C by a similar manner.

[0039]

#### Physical properties

Sheets of 2 mm in thickness were prepared by press curing at 120°C for 5 min and measured for physical properties according to JIS K 6301. Hardness was measured by A-type spring tester.

[0040]

Table I

	③ 組成物 No.	⑤ 保存日数 ⑥	硬化特性 ⑩	⑬ 物性			
			T10, T80 (秒) ⑪	硬さ (kgf/cm <sup>2</sup> ) ⑭	引張強さ (kgf/cm <sup>2</sup> ) ⑮	伸び (%) ⑯	引裂強さ (kgf/cm) ⑰
① 実施例 1	② 組成物 I	調製直後 ⑧	29.45	30	55	450	16
		10日 ⑦	29.45	—	—	—	—
② 比較例 1	④ 比較組成物 I	調製直後 ⑧	5.19	30	53	440	15
		10日 ⑦	測定不能 ⑫	—	—	—	—
① 実施例 2	③ 組成物 II	調製直後 ⑧	22.36	40	72	500	20
		1か月 ⑦	23.40	—	—	—	—
② 比較例 2	④ 比較組成物 II	調製直後 ⑧	25.40	39	70	510	18
		1か月 ⑦	測定不能 ⑫	—	—	—	—
① 実施例 3	③ 組成物 III	調製直後 ⑧	18.28	25	84	720	30
		3か月 ⑦	20.31	—	—	—	—
② 比較例 3	④ 比較組成物 III	調製直後 ⑧	20.32	24	85	750	33
		3か月 ⑦	66.95	—	—	—	—

Key: 1 Application Example  
 2 Comparative Example  
 3 Composition  
 4 Comparative composition  
 5 Number of days stored



6	As prepared
7	10 Days
8	One month
9	Three months
10	Curing characteristics
11	sec
12	Not measurable
13	Physical properties
14	Hardness
15	Tensile strength
16	Elongation
17	Tear strength

[0041]

As shown in Table I under curing characteristics, significant differences were observed between application examples and comparative examples. Composition I showed no changes in curing characteristics even after stored at 25°C for 10 days. On the other hand, comparative composition i gelled in 24 h when stored at 25°C. Also, composition II showed no changes in curing characteristics even after stored at 25°C for 1 month. On the other hand, comparative composition ii gelled in 24 h when stored at 25°C.

[0042]

Composition III showed no changes in curing characteristics even after 3 months when stored at 25°C. On the other hand, comparative composition iii showed poor curing characteristics at 150°C when stored 3 months at 25°C. After stored for 3 months at 25°C, the comparative composition iii showed increased plasticity and thin gelation on the surface.

[0043]

#### Effect of the invention

According to the present invention, heat-curable silicone elastomer compositions are provided having excellent storage stability, namely, good storage stability at room temperature over a long period of time, without loss of good curability at high temperature.